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TRACOR

SECOND QUARTERLY REPORT
AUGUST 17, 1962 - NOVEMBER 16, 1962

DEVELOPMENT OF A TRANSPARENT PRESERVATIVE
COMPOUND FOR AIRCRAFT STRUCTURAL METALS

for

Department of the Navy
Bureau of Naval Weapons
Washington 25, D. C.
Contract No. NOW 62-0549-C

December 14, 1962

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TRACOR, INC.

1701 Guadalupe St. Austin 1, Texas

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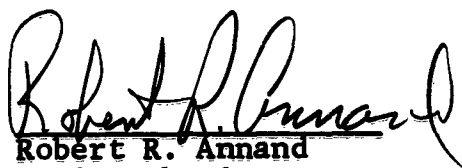
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Abstract

The major effort in this quarter was expended on reactions of amines with formaldehyde because the results of the previous quarter indicated that the greater reactivity of the formaldehyde and the greater freedom from side reaction inherent in its use would provide the means to obtain aliphatic hydrocarbon polymers containing the -N-C-N linkage. As a result of these experiments, four classes of products have been produced: (1) White, insoluble, infusible polymers have been obtained from reaction of piperazine and formaldehyde even under conditions which were designed to produce low molecular weights. These should not be crosslinked so their properties indicate a very high molecular weight. (2) Rubbery, somewhat hydrocarbon soluble polymers have been obtained from hexamethylenediamine and formaldehyde. Contrary to previous opinion, these have now been proved to be short chain, highly crosslinked polymers. (3) Low molecular weight polymers from cyclohexylamine and formaldehyde which are very soluble in cyclohexane were obtained. The backbone of these polymers is N-C-N-C-N-C-N-C. (4) A low molecular weight polymer from N,N'-diisopropylhexamethylenediamine and formaldehyde which exhibited very good hydrocarbon solubility has been obtained in a preliminary experiment. This polymer could be cast into a film but the film proved to be unstable when allowed to stand overnight in air. The amine reactant was synthesized in this laboratory and was chosen because it is expected to overcome the crosslinking problem encountered with hexamethylenediamine. As a result of the work to date, it is concluded that the N-C-N structure is indeed associated with good aliphatic hydrocarbon solubility. However, very high molecular weight, noncross-linked polymers are insoluble; short chain, highly crosslinked polymers have only very low solubility. What is needed is the

right combination of molecular weight (as high as possible with maybe a little crosslinking) and solubility. The work of the next quarter is directed toward obtaining medium-range molecular weights and possibly with just enough crosslinking to give good films but not enough to affect solubility.

I. INTRODUCTION

The object of this program is to obtain a transparent material which can be used as a protected coating for aircraft or missiles, and which can be easily removed without damage to underlying painted or plastic surfaces. This last need requires that the product material be highly soluble either in aliphatic hydrocarbons or in simple alcohols. Toward this end, it was proposed to study the reactions between carbonyl-containing compounds and amines in order to obtain polymeric materials containing the N-C-N linkage. Monomeric compounds containing this linkage are very soluble in aliphatic hydrocarbons.

Results obtained during the first quarter show that the reaction of ketones with diamines afford ketamine and enamine products in addition to polymer. These by-products are involved in the chain termination reactions and prevent the attainment of sufficient molecular size for the required end use. In addition, short chain diamines give monomeric cyclic by-products. When the more reactive aldehydes are used as the carbonyl reactant, encouraging solid products are obtained. The product from hexamethylenediamine and formaldehyde is sometimes found to be a clear, rubbery material with fair hydrocarbon solubility, but this product cannot be made reproducibly. In order to minimize or eliminate ketamine and enamine formation, numerous experiments were performed using piperazine and formaldehyde as reactants. The products obtained are insoluble powders, apparently of high molecular weight.

On the basis of these results, the work in this quarter has been concentrated in three areas: (1) a study of the piperazine-formaldehyde reaction with emphasis on ways and means to get lower molecular weights and thereby hydrocarbon solubility; (2) a study of the hexamethylenediamine-formaldehyde reaction to determine what procedures will reliably give useful products; and (3) a screening study of other carbonyl-amine systems which might have promise.

II. RESULTS OF THE WORK DURING THE SECOND QUARTER

A. The Piperazine-Formaldehyde Reaction

When formaldehyde is used as the carbonyl reactant, enamine formation is not possible because the molecule has no α hydrogen atoms. The use of a secondary amine eliminates the possibility of ketamine (Schiff's base) formation; and, if the diamine chosen is piperazine, no cyclic compounds can be formed. Thus, because very high molecular-weight products are expected from these reactants, and because the first quarter results showed that the product from these reactions is an insoluble and infusible powder, it is concluded that the products were high polymers. If a desirable material is to be obtained from this system, it will be necessary to limit the molecular weight so that practical levels of solubility can be reached.

There are three ways in which the molecular weight might be limited: (1) by replacement of some of the piperazine with a mono-secondary amine; (2) by replacement of some formaldehyde with a less reactive ketone or aldehyde; or (3) by intentional mismatching of the molar quantities of reactants used. Each of these methods was investigated but no useable polymers have yet been obtained. When 10 mole% of the piperazine was replaced with piperidine, the resulting material was a white powder, insoluble in benzene, but which fused with decomposition at about 250°C (in contrast to the previously obtained products which were infusible). Products obtained when part of the formaldehyde was replaced with acetone or when the molar quantities of reactants were intentionally mismatched did not differ appreciably from those obtained previously.

It was anticipated that polymers obtained with this system would have molecular weights in the 1000 range, a level which has afforded only liquid products when other amines were used. Because of their extreme insolubility in all solvents, it

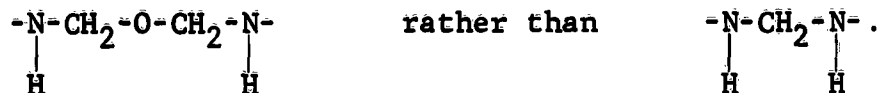
was not possible to measure the molecular weights readily. However, their chemical identity, established by careful collection of the water formed and by elemental analysis has been found to be consistent with the expected polymeric products. The properties of the resulting materials are not fully understood, but because the reaction cannot be controlled to give desirable products, no further work is planned with this reaction system at this time.

B. Hexamethylenediamine-Formaldehyde System

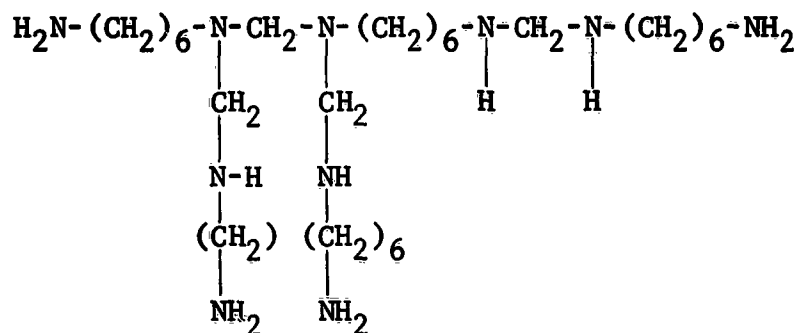
One of the advantages in using formaldehyde as the carbonyl reactant instead of a ketone is that ketamine and enamine formation is eliminated. Ketamine formation is possible, but the $-C=N-$ structure has never shown up in the IR spectra of the products from reactions using formaldehyde. By using hexamethylenediamine (or any primary diamine which has more than four chain methylene groups), formation of cyclic products is essentially eliminated and polymers containing recurring $-NH-CH_2-NH-$ groupings were expected.

Two different reaction media were used during the quarter. In aqueous solution, reaction of the amine with formaldehyde consistently gave an insoluble, slightly resilient polymer. All attempts to effect polymerization in aqueous media to achieve a hydrocarbon soluble polymer failed. In benzene, reaction of these compounds led either to moderately soluble liquid polymers or to insoluble, rubbery materials, and the results were difficult to duplicate. Evidently, the exact mole-ratio of reactants is critical. In some cases the product was inhomogeneous, being both liquid and solid. However, these materials became homogeneous when heated to about $150^{\circ}C$ for several hours. Some of the final products obtained in this way have shown moderate benzene solubility.

The infrared spectra of these polymers differ from expectations in that the N-C-N bands at 8.6, 8.8, and 9.0 microns are smeared together. It was previously assumed that this smearing of absorption bands and the low hydrocarbon solubility were due to polyacetal linkages in the polymer, i.e.,

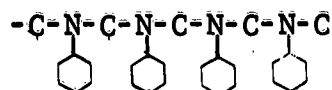


This does not fully explain the properties of the polymer, however, and other possible interpretations of the infrared spectra have been explored. The low hydrocarbon solubility and the nonreproducibility can both be explained if extensive crosslinking is occurring. This would lead to short, highly branched chains, as shown below:



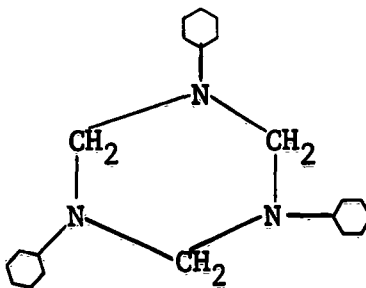
This hypothesis was tested in two different ways. A weighed amount of triethylenetetramine (a high-boiling amine containing both primary and secondary nitrogens) was heated to ca. 150°C and treated portionwise with a weighed amount of para-formaldehyde. The resulting polymer was an insoluble, rubbery material and the total amount of water produced in the reaction proved that all of the available active hydrogens were replaced.

In a second test of this hypothesis, an aqueous solution of a mono-primary amine (cyclohexylamine) was allowed to react with formaldehyde. If all the active hydrogens on the amine react, the following polymer should result:



A polymeric material separated from the water solution in about two hours. This material was an extremely viscous liquid and was very soluble in cyclohexane. The conclusion is that contrary to earlier ideas, secondary amino hydrogens do react and that these are producing crosslinked polymers in the hexamethylenediamine-formaldehyde system.

After a longer period of time, a second crystalline product separated from the cyclohexylamine-formaldehyde reaction mixture. According to molecular weight and infrared data, this proved to be the cyclic trimer shown below.



The same reactants in benzene solution yield only the trimer.

C. Screening for Promising Systems

Some representative amine-carbonyl systems which did not have the structural features which lead to insoluble or monomeric products were screened by carrying out reactions in both aqueous and nonaqueous media. The results of these experiments are contained in Table I. None of the systems produced

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TABLE I

AMINO CMPD	CARBONYL CMPD	REACTION SOLVENT	MOL. WT.	COMMENTS
Ethylenediamine (EDA)	Acetone	H ₂ O	---	No water insoluble product
Triethylenetetramine (TETA)	Acetone	H ₂ O	---	No water insoluble product
Hexamethylenediamine (HMDA)	Acetone	H ₂ O	---	No water insoluble product
Piperazine	Acetone	H ₂ O	---	No water insoluble product
EDA	Acetyl Acetone	H ₂ O	---	No water insoluble product
EDA	Acetonyl Acetone	H ₂ O	224	Orange crystalline cmpd, melting at 140°
EDA	Cyclohexanone	H ₂ O	---	No water insoluble product
EDA	Formaldehyde	H ₂ O	---	No water insoluble product
TETA	Formaldehyde	H ₂ O	---	No water insoluble product
HMDA	Formaldehyde	H ₂ O	Very high	Crosslinked polymer, see text
Piperazine	Formaldehyde	H ₂ O	High (?)	Intractable infusible powder
Piperazine and Piperidine	Formaldehyde	H ₂ O	High (?)	Intractable, but melts with decomposition >250°C
HMDA	Paraformaldehyde	H ₂ O	Very high	Insoluble polymer, in- distinguishable from formaldehyde-HMDA polymer
Piperazine	Paraformaldehyde	H ₂ O	Very high(?)	Intractable powder
HMDA	Acetaldehyde	H ₂ O	?	Rubbery, insoluble polymer formed in low yield
EDA	Isobutyraldehyde	H ₂ O	---	No insoluble product
EDA	Furfural	H ₂ O	---	No insoluble product

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TABLE I - CONTINUED

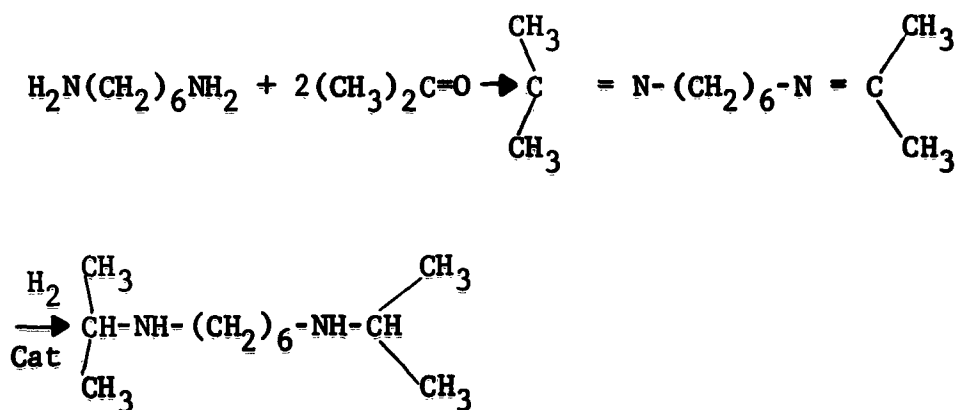
AMINO CMPD	CARBONYL CMPD	REACTION SOLVENT	MOL. WT.	COMMENTS
HMDA	Furfural	H ₂ O	---	No insoluble product
HMDA	Benzaldehyde	H ₂ O	---	No soluble product
Cyclohexylamine	Formaldehyde	H ₂ O	580	Very viscous liquid; very soluble in cyclohexane
			290	Cyclic trimer, see text
Cyclohexylamine	Paraformaldehyde	Benzene	---	Cyclic trimer only, no polymer
tert.butylamine	Formaldehyde	H ₂ O	---	No polymer recovered; some liquid product
Piperazine and Piperidine	Paraformaldehyde	Benzene	Very high	Indistinguishable from products made in aqueous media
N-aminoethylpiperazine	Paraformaldehyde	Benzene	?	Similar to HMDA polymers
N-aminoethylpiperazine	Formaldehyde	H ₂ O		
	Paraformaldehyde (2 moles/mole)	None	Very high	Crosslinked polymer
TETA				

a hydrocarbon soluble, film-forming polymer. However, the N-ethylaminopiperazine-formaldehyde reaction merits further work because the amine combines some of the features of both piperazine and hexamethylenediamine, and the products from these reactions do not exhibit the discouraging properties of the piperazine and hexamethylenediamine polymers.

The primary monoamines, other than cyclohexylamine, produced no interesting polymers. They were in the range of from 8-12 carbons however, and it is possible that shorter chain monoamines would produce better solubility. A small amount of additional work is contemplated to see if solubility can be improved this way.

D. Synthesis of N,N'-Diisopropylhexamethylenediamine

In order to prevent completely the crosslinking which has plagued us in the hexamethylenediamine-formaldehyde system, it is necessary to use a di-secondary amine. Commercial availability of such amines is limited to piperazine, so it is necessary to synthesize one. Because of the ease of synthesis and availability of the raw materials, N,N'-diisopropylhexamethylenediamine was synthesized according to the following scheme:



The over-all yield of N,N'-diisopropylhexamethylenediamine thus prepared was 65% with the major loss occurring during purification. It is anticipated that this amine will be used for the majority of future study.

III. FUTURE COURSE OF RESEARCH

On the basis of the results from this quarter's work, research in the immediate future is planned in the following three areas:

1. A small amount of effort will be expended on the polymerization of short chain mono-primary amines with formaldehyde to see if hydrocarbon solubility can be improved over the long chain monoamines.

2. The biggest portion of the total effort will be expended on the polymerization of N,N'-diisopropylhexamethylenediamine and formaldehyde, because the difficulties encountered with hexamethylenediamine are expected to be overcome by use of this compound.

3. Some of the effort will be expended on polymerization with formaldehyde of N-ethylaminopiperazine and mixtures of this amine with N,N'-diisopropylhexamethylenediamine in order to obtain a small amount of crosslinking and thereby improve film characteristics.